

FRENCH REPUBLIC

-----  
MINISTRY OF INDUSTRY

PATENT RIGHTS OFFICE

# PATENT

P.V. No. 27,322

No. 1,445,829

International Classification:

C 07 c

## New phenol purification process.

Company named: UNIVERSAL OIL PRODUCTS COMPANY, residing in the United States of America

Filed on August 5, 1965, at 3:04 pm, in Paris.

Issued by decree of June 6, 1966.

(Official Patent Rights Publication, No. 29 of 1966.)

(Patent application filed in the United States of America on August 5, 1964, under No. 387,787, in the name of Mr. Charles Vincent BERGER.)

This invention pertains to the purification of a phenol prepared by cleavage, catalyzed by an acid, hydroperoxide resulting from the oxidation of an aromatic alkyl hydrocarbon (sec.) and, in particular, the purification of phenol obtained by acid cleavage of hydroperoxide resulting from the oxidation of cumene.

The phenol is prepared through the partial oxidation of cumene into cumene hydroperoxide, followed by the cleavage of the hydroperoxide, catalyzed by an acid, in order to obtain a mixture resulting from the cleavage reaction, and containing phenol, acetone, as well as cumene that has not reacted. The mixture resulting from the cleavage reaction is neutralized and then subjected to fractionation in order to separate the produced phenol from the components with higher and lower boiling points of the mixture resulting from the cleavage reaction. Even with an efficient fractionating column, the phenolic fraction contains small, yet detrimental quantities of impurities formed as a result of the oxidation, cleavage, and phenol separation

operations. The impurities remaining in the phenolic fraction contain carbonylic compounds that include diacetone alcohol, hydroxyacetone, trimer acetone and, primarily, mesityl oxide, a condensation product of acetone that is virtually impossible to separate from phenol through simple distillation methods. The carbonylic compounds are detrimental, even in small quantities, as they tend to generate color, which makes the produced phenol unacceptable for a number of industrial applications.

The purpose of the invention is to eliminate virtually all impurities containing carbonylic compounds from a phenolic fraction collected from a reaction mixture resulting from the acid cleavage of the hydroperoxide obtained from the oxidation of an aromatic alkyl hydrocarbon (sec.) and, in particular, cumene.

The preparation of the phenol through the partial oxidation of cumene into cumene hydroperoxide, followed by the acid cleavage of hydroperoxide into phenol and acetone, is well known in the industry. The

process has been applied in the preparation of phenols in general, where an aromatic alkyl hydrocarbon (sec.) corresponding to the desired phenol is oxidized into hydroperoxide that is then subjected to cleavage in order to produce the desired phenol and an aliphatic ketone. Although this description pertains primarily to the purification of the phenolic fraction collected from a reaction mixture resulting from the acid cleavage of the hydroperoxide obtained from the oxidation of cumene, the process may also be used to eliminate the impurities that contain carbonylic compounds of a phenolic fraction collected from a reaction mixture resulting from the acid cleavage of the hydroperoxide obtained from the oxidation of an aromatic alkyl hydrocarbon (sec.) such as, for example, isopropyltoluene, m-isopropyltoluene, p-isopropyltoluene, p-diisopropylbenzene, sec. Butylbenzene, and  $\beta$ -isopropynaphthalene.

This invention pertains to a process for the purification of phenol that has been prepared through different stages that include the partial oxidation of an aromatic alkyl hydrocarbon (sec.) to form an alphahydroperoxidic derivate thereof, the cleavage of said derivate, catalyzed by an acid, to obtain a phenol and an aliphatic ketone, the neutralization of the mixture resulting from the cleavage reaction, and the separation of the reaction mixture neutralized from a fraction containing the phenol and the impurities that contain carbonylic compounds, with said process being characterized by the fact that at least part of said impurities are separated from the phenolic fraction by mixing  $H_2O$  with the fraction, bringing the mixture thus obtained into contact, at a high temperature, with a catalytic composite selected from the silica-alumina, silica-zirconia, alumina-zirconia, and silica-alumina-zirconia composites, which leads to the conversion of said carbonylic compounds into compounds with

lower boiling points, and said compounds are separated from the phenol by distillation.

Other objectives, advantages, and characteristics of the invention will appear in the detailed description that follows.

According to this process, water or steam is mixed with the phenolic fraction collected from the cleavage reaction mixture, and the water-phenol mixture is brought into contact with a catalytic composite, at a high temperature. The water-phenol mixture must contain at least 0.1 to 20% water, or steam corresponding to an equivalent quantity of water. This mixture is brought into contact with the catalytic composite described below, at a temperature of 150 to 250 °C. It is preferable to treat the phenol in the liquid phase, although there typically is some phenol in the vapor phase. Obviously, the optimal contact time is determined partly by the specific temperature used and partly by the catalytic composite used. A contact time equivalent to a liquid hourly space velocity of 0.1 to 5.0 and, preferably, 0.2 to 2.0, is adequate. Typically, a pressure ranging from the atmospheric pressure to 17 atmospheres is used, although the exact pressure is not critical.

The catalytic composites that may be used to implement the process according to the invention include, in particular, silica-alumina composites. The silica-alumina composites include the bentonite-type aluminum silicate base clays that have been activated by acid treatment. However, the silica-alumina composites prepared by synthesis, which contain 60 to 95% and, preferably, 70 to 90% silica, are the preferred catalytic composites. These composites are easily prepared by procedures known in the industry. One of these procedures consists in the coprecipitation or cogelation of the silica and alumina from a common solution. For example, aqueous solutions of sodium

silicate (standard liquid glass) and aluminum sulfate are mixed together, while adding a sufficient quantity of acid such as, for example, hydrochloric acid or sulfuric acid, so as to obtain a precipitate or a gel. Another procedure consists in impregnating a silica gel with an appropriate aluminum compound that can then be converted into alumina. For example, aluminum hydroxide is precipitated from an aqueous solution of an appropriate aluminum salt such as aluminum sulfate, in the presence of silica gel that is immersed in the solution. The composite thus obtained is then heated at a high temperature and the impregnated hydroxide is converted into alumina by thermal decomposition. Alternatively, the silica gel may be impregnated with a decomposable aluminum salt that produces alumina when subsequently heated. The aluminum nitrate is appropriate for this purpose and can impregnate the silica gel when the gel is immersed in an aqueous solution of aluminum nitrate.

Typically, the silica and alumina base composite prepared according to the procedures described above is washed with water so as to separate the soluble salts, and it is then dried, generally at a temperature ranging from 95 to 200 °C. The composite then undergoes calcination at a temperature of at least 475 °C and, typically, at a temperature ranging from a minimum of 475 to 800 °C. The preferred temperature is comprised between 600 and 700 °C. The calcination may be carried out in any appropriate atmosphere. Generally, the calcination is carried out in the presence of air or another oxidizing medium, although it may also be carried out in a reducing atmosphere such as hydrogen, for example, or in an inert atmosphere such as nitrogen, for example.

Although the silica-alumina type is a preferred catalytic composite, other composites, i.e. the silica-zirconia, alumina-

zirconia, and silica-alumina-zirconia types, exhibit desirable catalytic characteristics and may also be used.

The treatment of the phenolic fraction with water and by bringing it into contact with the silica-alumina catalyst, for example, can be carried out in two separate stages or in a single stage. By using the process described herein, the impurities that contain carbonylic compounds are converted into conversion products with lower boiling points, which are easily separated from the phenol by distillation or by an entrainment gas such as nitrogen, or by a combination of both entrainment and distillation operations. The other impurities that could be present are incidentally separated as a result of the process according to this invention. For example, when the excess water is separated from the phenol by distillation methods, the methyl benzofuran that is typically present at least in trace amounts is collected as a portion of the steam distillate.

The following examples are given as illustrations of the invention.

*Examples I and II.* – Some phenol obtained by fractional distillation from a neutralized reaction mixture resulting from the cleavage of cumene hydroperoxide is analyzed by gas-liquid chromatography, which makes it possible to determine that it contains mesityl oxide. The phenol, which is intimately mixed with steam, is loaded into a vertical tube-in-shell reactor that contains 200 cm<sup>3</sup>, or 120g, of 3.2mm silica-alumina pellets containing 88% silica and 12% alumina, that are deposited into said reactor on a fixed bed. The reactor is maintained at near atmospheric pressure and at a temperature of 190 °C, and the phenol and steam feed rate is adjusted so as to obtain streams with variable quantities of water. The effluent of the reactor is continuously removed from the reactor and cooled. The analysis of the load and products, as reported below, indicates a substantial

conversion of mesityl oxide into acetone, which is easily separated by distillation.

	Examples	
	I	II
Loading rate, cm <sup>3</sup> /hour .....	40	100
Water, wt. % .....	2.0	5.0
Analysis of load, wt. %:		
Acetone .....	0.0010	0.0010
Mesityl oxide.....	0.1940	0.1940
Analysis of product, wt. %:		
Acetone .....	0.1467	0.1193
Mesityl oxide.....	0.0060	0.0041

*Examples III and IV.* - A phenolic fraction obtained by distillation of a neutralized reaction mixture resulting from the cleavage of cumene hydroperoxide, and containing carbonylic impurities, primarily mesityl oxide, but also diacetone alcohol, hydroxyacetone and trimer acetone, is treated so as to convert the complex carbonylic compounds into acetone. The phenolic fraction is mixed with approximately 10% water, by weight. Then the phenol is loaded through a steam-heated pipe into a vertical tube-in-shell reactor, at a liquid hourly space velocity of 0.5, with the reactor containing 100 cm<sup>3</sup> of silica-alumina pellets that contain 76% silica and 24% alumina, on a fixed bed. The reactor is maintained at a pressure of approximately 5 atmospheres and at a temperature of 205 °C. The load and product analyses reported below show the formation of other miscellaneous compounds more volatile than phenol which, once again, can be separated by distillation.

	Examples	
	III	IV
Analysis of load, wt. %:		
Acetone .....	0.0036	0.0036
Mesityl oxide.....	0.1489	0.1489
Miscellaneous.....	0.0915	0.0915
Analysis of product, wt. %:		
Acetone .....	0.1788	0.1606
Mesityl oxide.....	0.0063	0.0067
Miscellaneous.....	0.1349	0.1868

*Example V.* - A phenolic fraction obtained by distillation from a neutralized reaction mixture resulting from the cleavage of cumene hydroperoxide and containing acetone polymers, is converted into a phenolic product that contains separable impurities, by using a silica-zirconia composite containing approximately 90% silica as a catalyst. A quantity of 200 cm<sup>3</sup> of the catalyst in the form of 3.2 mm spheres is laid on a fixed bed in a vertical tube-in-shell reactor. The phenol is loaded into the reactor at the same time as the steam, in order to form a water-phenol load containing approximately 5% water, by weight. The water-phenol mixture is loaded at a liquid hourly space velocity of approximately 1, with the reactor being maintained at a temperature of about 190 °C and at a pressure of approximately 3.4 atmospheres. The reactor effluent is collected and analyzed, as provided below:

Analysis of load, wt. %:	
Acetone .....	0.01
Mesityl oxide.....	0.16
Miscellaneous.....	0.14

Analysis of product, wt. %:	
Acetone .....	0.18
Mesityl oxide.....	0.01
Miscellaneous.....	0.03

The method of analysis used in this example is less accurate. However, the conversion of mesityl oxide into acetone is almost complete.

Of course, the invention is not limited to the procedures described above, which were only provided as examples.

#### SUMMARY

The purpose of the invention is a process for the purification of phenol that has been prepared through different stages that include the partial oxidation of an aromatic alkyl hydrocarbon (sec.) to form an alphahydroperoxidic derivate thereof, the cleavage of said derivate, catalyzed by an acid, to obtain a phenol and an aliphatic ketone, the neutralization of the mixture resulting from the cleavage reaction, and the separation of the reaction mixture neutralized from a fraction containing the phenol and the impurities that contain carbonylic compounds, with said process being unique due, in particular, to the following characteristics, whether considered individually or as in combinations:

1. At least part of said impurities are separated from the phenolic fraction by mixing H<sub>2</sub>O with the fraction, bringing the mixture thus obtained into contact, at a high temperature, with a catalytic composite selected from the silica-alumina, silica-zirconia, alumina-zirconia, and silica-alumina-zirconia composites, which leads to the conversion of said carbonylic

compounds into compounds with lower boiling points, and said compounds are separated from the phenol by distillation;

2. The phenolic fraction mixed with H<sub>2</sub>O is brought into contact with a catalytic composite consisting of silica and alumina;

3. The phenolic fraction to be purified was collected from a reaction mixture resulting from the acid cleavage of hydroperoxide obtained by the oxidation of cumene;

4. The phenolic fraction to be purified is mixed with 0.1 to 20% by weight of H<sub>2</sub>O, and the mixture thus obtained is brought into contact with the catalytic composite, at a temperature of 150 to 250 °C;

5. The mixture of H<sub>2</sub>O and phenolic mixture to be purified is brought into contact with the catalytic composite at a liquid hourly space velocity of 0.1 to 5.0;

6. The phenolic fraction mixed with H<sub>2</sub>O is brought into contact with a catalytic composite constituted by silica and alumina, and containing 60 to 85% silica.

Company named:  
UNIVERSAL OIL PRODUCTS COMPANY  
By proxy:  
Cabinet LAVOIX